Per and Polyfluorinated Compounds: Health and Environmental Impacts

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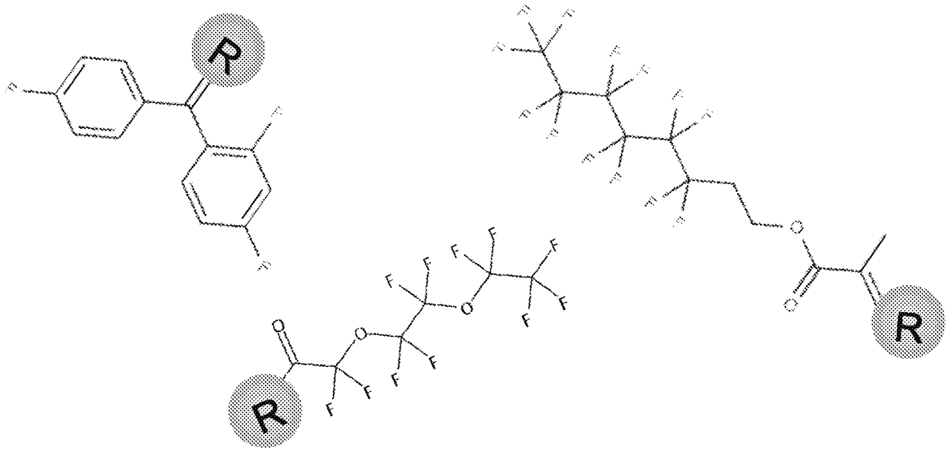

Highly Fluorinated Chemicals in Food Packaging Symposium
University of California at Berkeley
February 9, 2017

Green Science Policy Institute

Presentation Outline

- Introduce per- and polyfluoroalkyl substances (PFAS)
  - what are they?
- Discuss chemical properties of PFAS
  - why are they useful?
- Review what is known about routes of human exposure
- Some recent findings
- Describe animal and human health effects of PFAS
- Long-term outlook regarding PFAS

Major Considerations

According to *Commission of the European Communities: (2000)* uses the Principle of Precaution…"where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost effective measures to prevent environmental degradation". *http://ec.europa.eu/dgs/health_consumer/library/pub/pub07_en.pdf*

Green Chemistry…always strive to use the least toxic alternative available, with a preference for compounds that quickly and harmlessly degrade to their original starting materials
Anastas PT, Warner JC. 1998. Green Chemistry: Theory and Practice. New York, NY Oxford University Press

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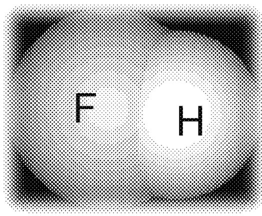
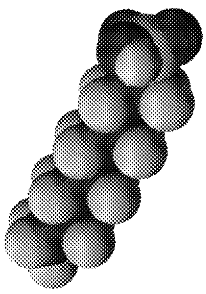
Per- and Polyfluoroalkyl Substances (PFAS)

- Synthetic analogs to long chain fatty acids – but fluorine is used in the place of hydrogen
- PFAS are entirely manmade – no natural sources and literally thousands of different formulations in use
- Many PFAS are extraordinarily persistent in the environment, cannot be broken down by natural systems





PFOS

- PFAS are detected in all environmental media – air, water, soil, sludge
- Like other persistent organic pollutants, many PFAS bio-accumulate in animals at the top of the food chain – birds, fish, livestock, and humans
- Environmental persistence leads to global distribution via air and water movement – releases here can be significant for communities on the other side of the world

Some Per- and Polyfluoroalkyl Substances (PFAS)

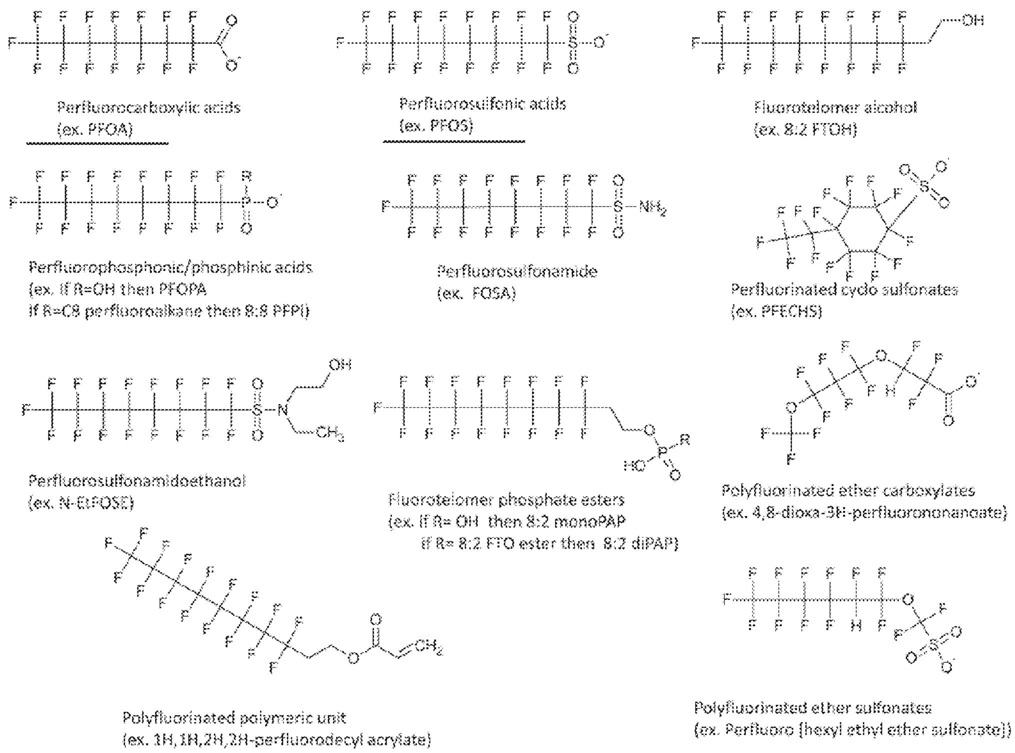


Figure 1. Generic structures for polyfluorinated compounds. The $n = 8$ linear carbon structures are shown for many of these examples, but $n = 4-14$ linear and/or branched carbon units are generally possible.

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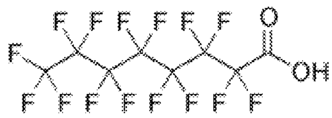
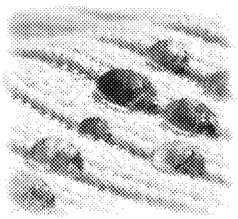
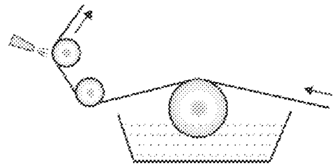
Deliberative Process / Ex. 5

PFAS Are Used In Many Products







Textile treatments

Paints

Pesticides

Floor/Ski polish

Denture cleaner

Polymers

Adhesives

Lubricant additive

Paper coatings

Surfactants

Fire-fighting foam

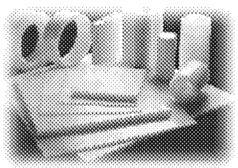
Photographic film

Mining fluids

Non-stick cookware

Caulks

Carpets



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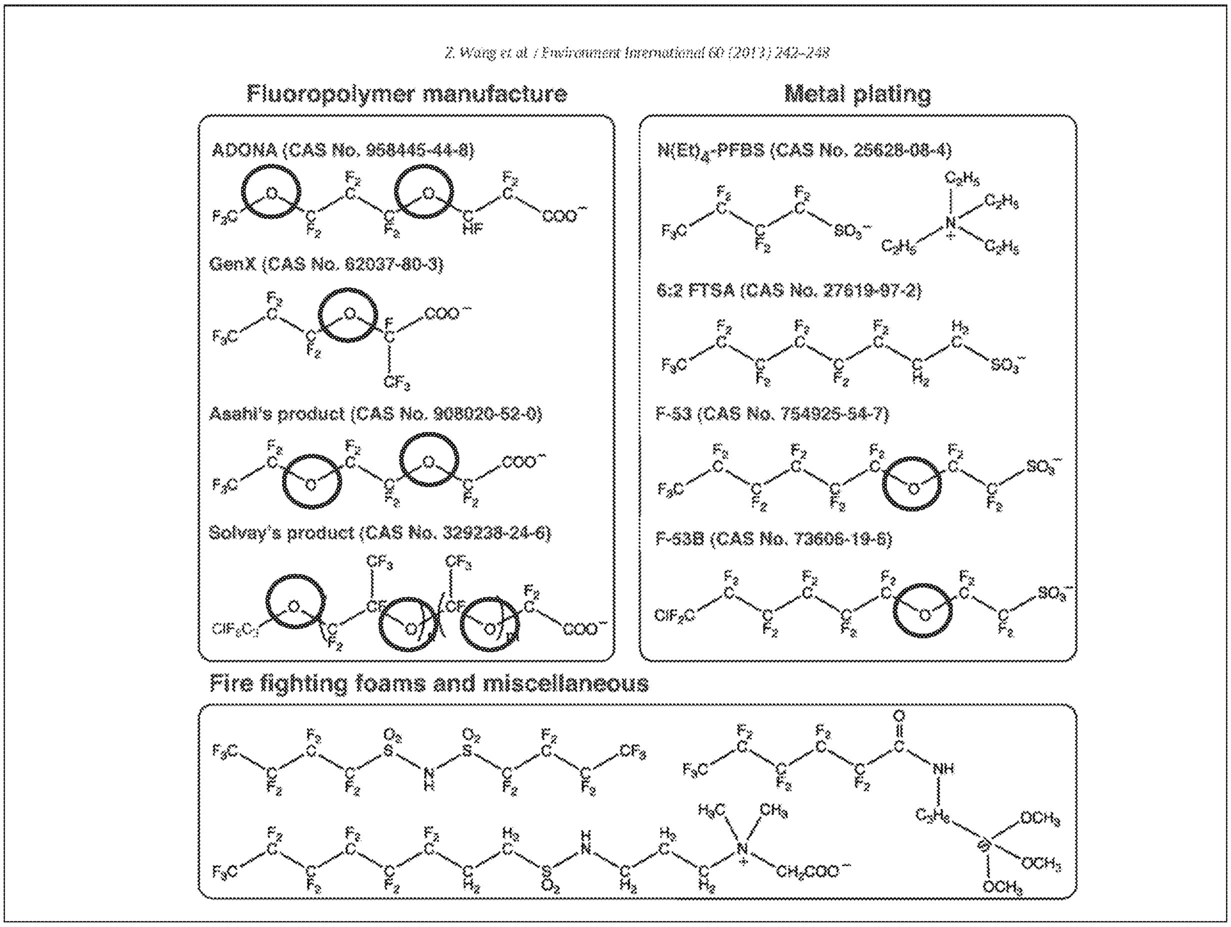
Deliberative Process / Ex. 5



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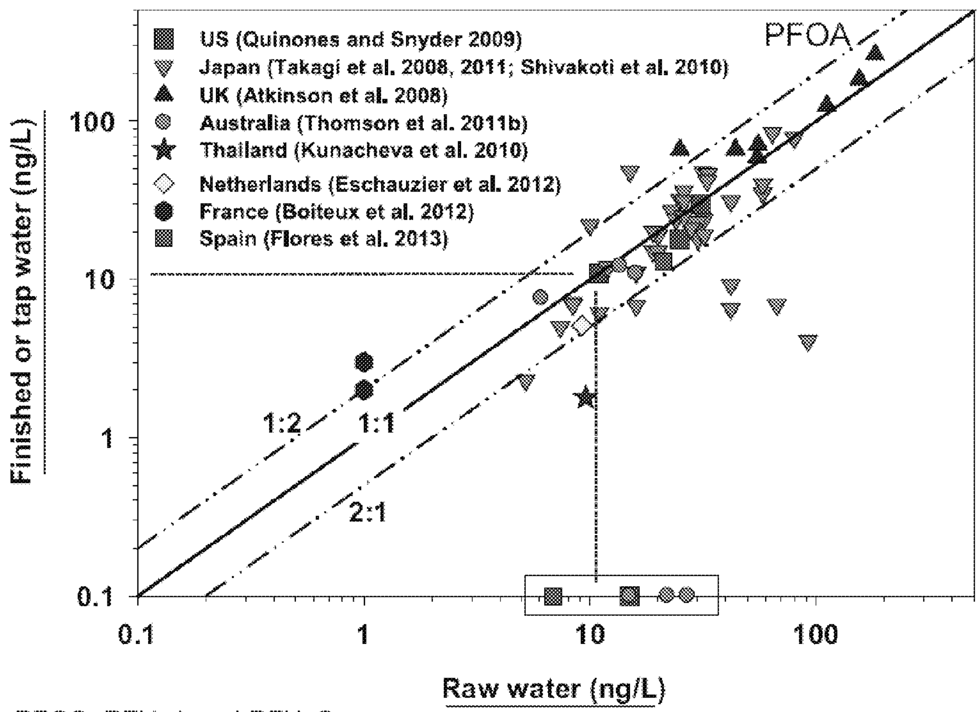
Deliberative Process / Ex. 5

Sources of PFAS Exposure for Humans

- Best documented source is contaminated drinking water near industrial production facilities or waste disposal e.g., Cottage Grove, Minnesota; Parkersburg, West Virginia; Dalton, Georgia; Decatur, Alabama; Arnsberg, Germany; Osaka, Japan *Lindstrom et al. 2011, Environ. Sci. & Technol. (45) 8015 – 8021*
- Food is also implicated in many studies, especially fish from contaminated waters, items contaminated by food packaging and breast milk *Fromme et al. 2009, Inter. J. Hyg. & Envr. Heath (212) 239-270; Mogensen et al. 2015, Environ. Sci. & Technol. (49) 10466 - 10473*
- House dust may also be an important route of exposure – especially for children who ingest relatively higher levels of dust via hand-to-mouth activity *Shoeib et al. 2011, Environ. Sci. & Technol. (45) 7999 - 8005*
- Workplace exposures significant for some sectors: manufacturing or services making or directly using PFAS, apparel sales, waste treatment *Nilsson et al. 2013 Environ. Sci.: Processes Impacts, 15, 814-822*

PFAS Removal Efficiency



Similar for PFOS, PFHxA and PFHxS

Rahman et al., (2014) *Water Research,* 50:318-340

Deliberative Process / Ex. 5

Environmental Science & Technology Letters

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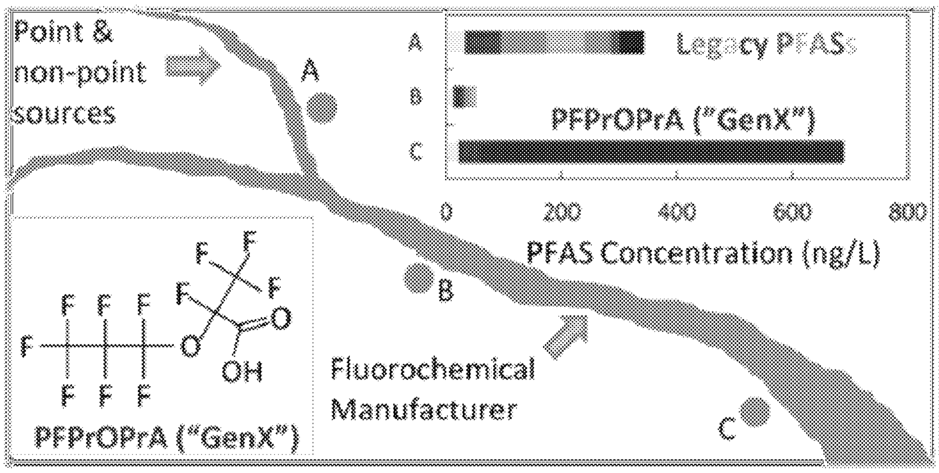
Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,[*,†,‡,⊗] Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,[∥] Ben Kearns,[∥] Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]



Environmental Science & Technology
Article
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Novel Polyfluorinated Compounds Identified Using High Resolution Mass Spectrometry Downstream of Manufacturing Facilities near Decatur, Alabama

Seth Newton,[†] Rebecca McMahen,[‡] James A. Stoeckel,[§] Michael Chislock,[§] Andrew Lindstrom,[†] and Mark Strynar*,[†]

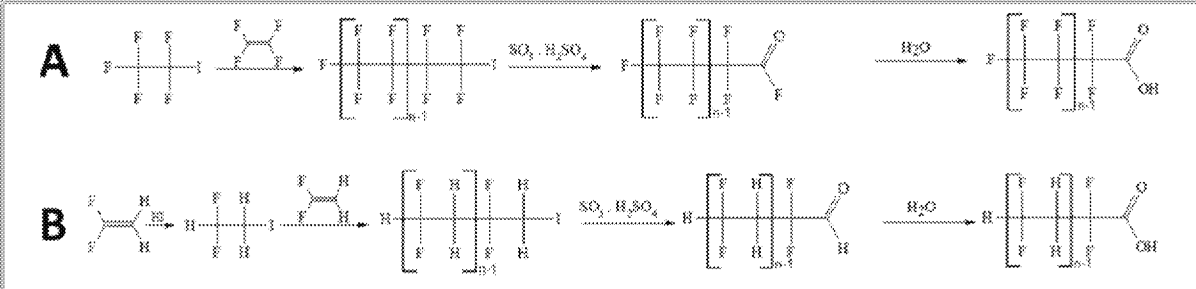
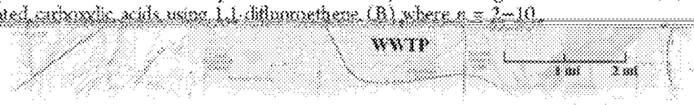


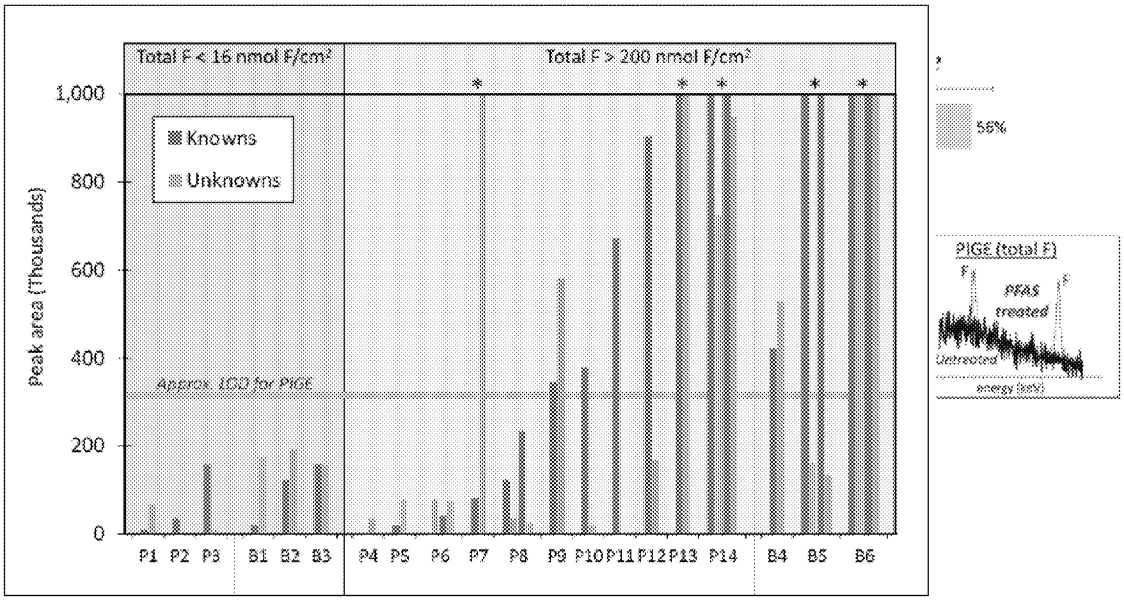
Figure 3. Synthesis reaction for the production of a traditional perfluorinated carboxylic acid using tetrafluoroethene (A) and the hypothesized synthesis of the proposed polyfluorinated carboxylic acids using 1,1-difluoroethene (B) where $n = 2-10$.



Environmental Science & Technology Letters
Letter
pubs.acs.org/journal/estlcu

Fluorinated Compounds in U.S. Fast Food Packaging

Laurel A. Schaider,[*,†] Simona A. Balan,[‡] Arlene Blum,[§,∥] David Q. Andrews,[⊥] Mark J. Strynar,[#] Margaret E. Dickinson,[∇] David M. Lunderberg,[∇] Johnsie R. Lang,[○] and Graham F. Peaslee[⊗]



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Inventory of Effective Food Contact Substance (FCS) Notifications

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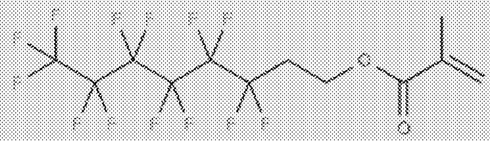
Records Found: 66 Show All Page 1 of 2

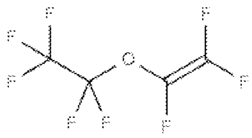
FCN No. (sorted Z-A)	Food Contact Substance	Manufacturer/Supplier	Effective Date
1676	2-propenoic acid, 2-methyl-, 2-hydroxyethyl ester, polymer with 2-propenoic acid and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-methyl-2-propenoate, sodium salt (CAS Reg. No. 1876204-24-0).	Asahi Glass Co., Ltd. AGC Chemicals Americas, Inc.	Sep 21, 2016
1674	3,4,4'-Trifluorobenzophenone (TFBP) (CAS Reg. No. 80512-44-3).	Victrex Plc	Sep 2, 2016
1661	D-Glucitol, 1-deoxy-1-(methylamino)-, reaction products with 4-ethenylphenol homopolymer and formaldehyde, 1-hydroxyethylidene-1,1-diphosphonic acid, manganous oxide, phosphate, fluorotitanic and fluorozirconic salts. **REPLACES FCN 1472**	Henkel Adhesive Technologies	Jul 20, 2016
1601	2,3,3,4,4,5,5-Heptafluoro-1-pentene polymer with ethene and tetrafluoroethene (CAS Reg. No. 94228-79-2) .	Daikin Industries, LTD	Mar 5, 2016
1560	Vinylidene fluoride-hexafluoropropene copolymer (CAS Reg. No. 9011-17-0).	Arkema, Inc.	Sep 18, 2015
1493	Copolymer of 2-(dimethylamino) ethyl methacrylate with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate, N-oxide, acetate (CAS Reg. 1440528-04-0)	Archroma Management GmbH	Dec 31, 2014
1451	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymer with 1-ethenyl-2-pyrrolidinone and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-propenoate, acetate (CAS Reg. No. 1334473-84-5).	Daikin America, Inc.	Sep 4, 2014

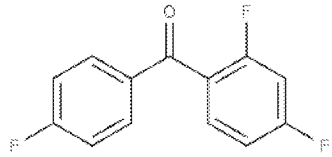
http://www.accessdata.fda.gov/scripts/fdcc/index.cfm?set=FCN&sort=FCN_No&order=DESC&startrow=1&type=basic&search=fluoro

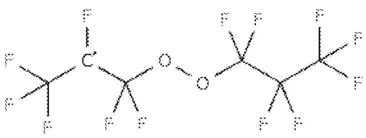
“Fluoro” Substructures in Database

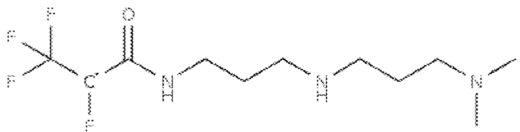
n=23 include











PFAS Health Effects Summary

- These chemicals not only persist in the environment, but also inside the body once ingested, particularly in humans

Serum half-life	PFBS (C4)	PFHxS (C6)	PFOS (C8)	PFBA (C4)	PFHxA (C6)	PFOA (C8)	PFNA (C9)
Mouse	5 hours	30 days	40 days	12 hours	2 hours	20 days	60 days
Humans	28 days	8.5 years	4-5 years	3 days	32 days	3-4 years	unknown

- Some of these chemicals are more potent than the others, but all of them have the similar effects

	PFBA (C4)	PFPeA (C5)	PFHxA (C6)	PFHpA (C7)	PFOA (C8)	PFNA (C9)	PFDA (C10)
Mouse	1.0	1.1	1.3	4.6	8.5	10.2	2.6
Humans	1.0	1.4	1.6	5.0	6.5	6.8	--

- Laboratory results suggest that PFAS effects are additive

Profiles of PFAS Toxicity and Adverse Health Effects

- Liver and Metabolic toxicity
  - *Mouse:* enlarged and fatty liver, decreased serum cholesterol, triglycerides
  - *Humans:* increased serum cholesterol, uric acid
- Reproductive and Developmental Toxicity
  - *Mouse:* neonatal mortality, low birth weight, growth deficits, developmental delays
  - *Humans:* preeclampsia, low birth weight and small size, delayed onset of puberty
- Tumor Induction
  - *Mouse:* liver, pancreas and testes
  - *Humans:* kidney and testes
- Immunotoxicity
  - *Mouse:* atrophy of thymus and spleen, suppressed immune responses
  - *Humans:* reduced immune responses to vaccines in children
- Endocrine Disruption
  - *Mouse:* reduced serum thyroid hormones
  - *Humans:* slight elevation of serum thyroid hormones
- Neurotoxicity
  - *Mouse: a* few reports of neuronal deficits and behavioral abnormalities
  - *Humans:* some reports of learning disability

Newer PFAS: Summary of what is Known?

Most compounds have limited but growing toxicology testing for some PFAS Gordon et al., (ADONA), Rae et al., (GenX), Dewitt et al., (GenX), Serex et al., 2014 (6:2 FTOH), Danish EPA 2015 (short-chain PFAS) BUT no information on others (Strynar et a., 2015, Newton et al., 2016, Schaider et al., 2017)

Toxicology found to be "more favorable" than longer chain PFAS (Dupont GenX brochure) but NOT non-toxic (Rae et al., 2015 (GenX); Gordon et al., (ADONA), Serex et al., 2014 (6:2 FTOH)

Shorter chain length PFAS are: almost completely absorbed orally (Chang et al., 2008 (PFBA), Olsen et al., 2009 (PFBS) and Gannon et al., 2011 (PFHxA) more rapidly eliminated in mammals Gannon et al., 2016 (GenX) and poorly attenuated in Traditional drinking water systems (Sun et al., 2016)

Environmental bio-concentration of shorter chain length is of low concern (Hoke et al., (GenX), BUT has been shown to occur in fish species (Chu et al., 2016., (FBSA)

Terminal per- and polyfluorinated metabolites are recalcitrant Danish EPA 2015 (short-chain PFAS), Wang et al., 2013 (PFPEs), ECHA 2015

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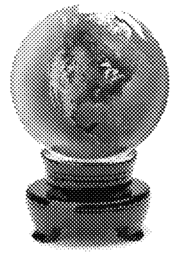
Future Perspectives



- Demand for PFAS performance chemicals increasing with a shift in production of "legacy" materials to the developing world (India, Poland, China, Russia)
- New generation of "replacement" PFAS now being produced in the industrialized world, but their identity and health effects are relatively unknown.
- Environmental and health effects research on "replacement" PFAS now underway – preliminary results suggest they have similarity to legacy compounds
- New research on human exposure of PFAS and their adverse health effects, as well as their ecological impacts will support risk assessment and regulatory decisions
- Virtually every person has PFAS in their blood – biomonitoring studies will inform the trends of change in the future regarding new and legacy chemicals

Questions?

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